

STABILIZED ESTER PEROXYCARBOXYLIC ACID COMPOSITIONS

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This application claims priority under 35 U.S.C. §119(e) to U.S. Provisional Application Serial Number 60/274,885, filed on March 9, 2001, which is incorporated by reference herein.

Field of the Invention

10 The present invention relates to stabilized compositions of an ester peroxycarboxylic acid, methods employing these stabilized compositions, and methods of making these compositions. Typically, the stabilized compositions include a C₂ or higher alcohol.

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Background of the Invention

15 Ester peroxycarboxylic acid compositions exhibit useful antimicrobial activity. Synthesis of ester peroxycarboxylic acids is known, as is their use as antimicrobial agents in cleaning products and methods. Existing compositions including ester peroxycarboxylic acids suffer from unacceptable decomposition of the ester peroxycarboxylic acid, or unacceptable stabilizing agents in the composition.

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Summary of the Invention

The present invention relates to stabilized compositions of an ester peroxycarboxylic acid, methods employing these stabilized compositions, and methods of making these compositions. Typically, the stabilized compositions include a C₂ or higher alcohol.

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In one embodiment, the stabilized composition of an ester peroxycarboxylic acid includes an ester peroxycarboxylic acid and a C₂ or higher alcohol effective for stabilizing the ester peroxycarboxylic acid at non-toxic concentration of the alcohol. The C₂ or higher alcohol can include a mono-, di-, or tri- hydric alcohol, such as a straight chain or branched aliphatic or C₂-C₁₂ hydroxy derivative, for example, ethanol, n-propanol, iso-propanol, n-butanol, sec-butanol, iso-butanol, n-pentanol, propylene glycol, butylene glycol, hexylene glycol, glycerine, polyethylene glycol, polypropylene glycol, polybutylene glycol, and the like, or a combination thereof. The C₂ or higher alcohol can be present at effective

concentrations in the range of about 1 wt-% to about 80 wt-%. The composition can also include a surfactant and/or a buffer.

In another embodiment, the invention includes a method employing the stabilized composition of the invention to reduce a population of one or more microorganisms on an object, such as on a surface or in a fluid. In an embodiment, the invention includes a method employing the stabilized composition of the invention to reduce the population of a microorganism on skin or to treat a disease of skin. In an embodiment, the invention includes a method employing the stabilized composition of the invention to reduce an odor of an object, such as of a surface or of a fluid. In an embodiment, the invention includes a method employing the stabilized composition of the invention to bleach an object. These methods include contacting the object with a stabilized ester peroxy carboxylic acid composition of the invention. Contacting can include spraying the composition, immersing the object in the composition, foam or gel treating the object with the composition, or a combination thereof.

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Detailed Description of the Invention

Definitions

As used herein, the term "alcohol" refers to a broad class of hydroxyl-containing organic compounds. Alcohols include monohydric, dihydric, trihydric, and polyhydric alcohols. Monohydric alcohols include aliphatic, alicyclic, aromatic, heterocyclic, or polycyclic alcohols. Aliphatic alcohols include paraffinic and olefinic alcohols. Dihydric alcohols, also known as diols, have two hydroxyl groups and include glycols and other derivatives. Trihydric alcohols have three hydroxyl groups and include glycerol and its derivatives. Polyhydric alcohols are also known as polyols.

25 As used herein, the term "C₂ or higher alcohol" refers to alcohols with more than 1 carbon atom, e.g., 2 or more carbon atoms. This term excludes methanol. C₂ or higher alcohols include monohydric, dihydric, trihydric, and polyhydric alcohols with more than 1 carbon atom. Monohydric alcohols with more than 1 carbon atom include aliphatic, alicyclic, aromatic, heterocyclic, or polycyclic alcohols with more than 1 carbon atom.
30 Aliphatic alcohols with more than 1 carbon atom include paraffinic and olefinic alcohols with more than 1 carbon atom. Dihydric alcohols, also known as diols, with more than 1

carbon atom have two hydroxyl groups and include glycols and other derivatives. Trihydric alcohols with more than 1 carbon atom have three hydroxyl groups and include glycerol and its derivatives. Polyhydric alcohols with more than 1 carbon atom are also known as polyols with more than 1 carbon atom. Alcohols with more than 1 carbon atom can also be referred 5 to as hydroxy alkyl derivatives.

As used herein, the term "microorganisms" refers to any noncellular or unicellular (including colonial) organism. Microorganisms include all prokaryotes. Microorganisms include bacteria (including cyanobacteria), lichens, microfungi, protozoa, viruses, viroids, viruses, and some algae. As used herein, the term "microbe" is synonymous with 10 microorganism.

As used herein, the term "object" refers to a something material that can be perceived by the senses, directly and/or indirectly. Objects include a surface, including a hard surface (such as glass, ceramics, metal, natural and synthetic rock, wood, and polymeric), an elastomer or plastic, woven and non-woven substrates, a food processing surface, a health care surface, and the like. Objects also include a food product (and its surfaces); a body or stream of water or a gas (e.g., an air stream); and surfaces and articles employed in 15 hospitality and industrial sectors.

As used herein, the phrase "food product" includes any food substance that might require treatment with an antimicrobial agent or composition and that is edible with or without further preparation. Food products include meat (e.g. red meat and pork), seafood, 20 poultry, fruits and vegetables, eggs, living eggs, egg products, ready to eat food, wheat, seeds, roots, tubers, leafs, stems, corms, flowers, sprouts, seasonings, or a combination thereof. The term "produce" refers to food products such as fruits and vegetables and plants or plant-derived materials that are typically sold uncooked and, often, unpackaged, and that 25 can sometimes be eaten raw.

As used herein, the phrase "plant product" includes any plant substance or plant-derived substance that might require treatment with an antimicrobial agent or composition. Plant products include seeds, nuts, nut meats, cut flowers, plants or crops grown or stored in a greenhouse, house plants, and the like. Plant products include many animal feeds.

As used herein, a processed fruit or vegetable refers to a fruit or vegetable that has 30 been cut, chopped, sliced, peeled, ground, milled, irradiated, frozen, cooked (e.g., blanched,

pasteurized), or homogenized. As used herein a fruit or vegetable that has been washed, colored, waxed, hydro-cooled, refrigerated, shelled, or had leaves, stems or husks removed is not processed.

As used herein, the phrase "meat product" refers to all forms of animal flesh,
5 including the carcass, muscle, fat, organs, skin, bones and body fluids and like components
that form the animal. Animal flesh includes the flesh of mammals, birds, fishes, reptiles,
amphibians, snails, clams, crustaceans, other edible species such as lobster, crab, etc., or
other forms of seafood. The forms of animal flesh include, for example, the whole or part of
animal flesh, alone or in combination with other ingredients. Typical forms include, for
10 example, processed meats such as cured meats, sectioned and formed products, minced
products, finely chopped products, ground meat and products including ground meat, whole
products, and the like.

As used herein, the term "poultry" refers to all forms of any bird kept, harvested, or
domesticated for meat or eggs, and including chicken, turkey, ostrich, game hen, squab,
15 guinea fowl, pheasant, quail, duck, goose, emu, or the like and the eggs of these birds.
Poultry includes whole, sectioned, processed, cooked or raw poultry, and encompasses all
forms of poultry flesh, by-products, and side products. The flesh of poultry includes muscle,
fat, organs, skin, bones and body fluids and like components that form the animal. Forms of
animal flesh include, for example, the whole or part of animal flesh, alone or in combination
with other ingredients. Typical forms include, for example, processed poultry meat, such as
20 cured poultry meat, sectioned and formed products, minced products, finely chopped
products and whole products.

As used herein, the phrase "food processing surface" refers to a surface of a tool, a
machine, equipment, a structure, a building, or the like that is employed as part of a food
25 processing, preparation, or storage activity. Examples of food processing surfaces include
surfaces of food processing or preparation equipment (e.g., slicing, canning, or transport
equipment, including flumes), of food processing wares (e.g., utensils, dishware, wash ware,
and bar glasses), and of floors, walls, or fixtures of structures in which food processing
occurs. Food processing surfaces are found and employed in food anti-spoilage air
30 circulation systems, aseptic packaging sanitizing, food refrigeration and cooler cleaners and
sanitizers, ware washing sanitizing, blancher cleaning and sanitizing, food packaging

materials, cutting board additives, third-sink sanitizing, beverage chillers and warmers, meat chilling or scalding waters, sanitizing gels, cooling towers, food processing antimicrobial garment sprays, and non-to-low-aqueous food preparation lubricants, oils, and rinse additives.

5 As used herein, the phrase “air streams” includes food anti-spoilage air circulation systems. Air streams also include air streams typically encountered in hospital, surgical, infirmity, birthing, mortuary, and clinical diagnosis rooms.

As used herein, the term “waters” includes food process or transport waters. Food process or transport waters include produce transport waters (e.g., as found in flumes, pipe transports, cutters, slicers, blanchers, retort systems, washers, and the like), belt sprays for food transport lines, boot and hand-wash dip-pans, third-sink rinse waters, and the like.

10 Waters also include domestic and recreational waters such as pools, spas, recreational flumes and water slides, fountains, and the like.

As used herein, the phrase “health care surface” refers to a surface of an instrument, a device, a cart, a cage, furniture, a structure, a building, or the like that is employed as part of a health care activity. Examples of health care surfaces include surfaces of medical or dental instruments, of medical or dental devices, of electronic apparatus employed for monitoring patient health, and of floors, walls, or fixtures of structures in which health care occurs.

Health care surfaces are found in hospital, surgical, infirmity, birthing, mortuary, and clinical diagnosis rooms. These surfaces can be those typified as “hard surfaces” (such as walls, floors, bed-pans, etc.,), or woven and non-woven surfaces (such as surgical garments, draperies, bed linens, bandages, etc.,), or patient-care equipment (such as respirators, diagnostic equipment, shunts, body scopes, wheel chairs, beds, etc.,), or surgical and diagnostic equipment. Health care surfaces include articles and surfaces employed in animal 25 health care.

As used herein, the term “instrument” refers to the various medical or dental instruments or devices that can benefit from cleaning with a stabilized composition according to the present invention.

As used herein, the phrases “medical instrument”, “dental instrument”, “medical 30 device”, “dental device”, “medical equipment”, or “dental equipment” refer to instruments, devices, tools, appliances, apparatus, and equipment used in medicine or dentistry. Such

instruments, devices, and equipment can be cold sterilized, soaked or washed and then heat sterilized, or otherwise benefit from cleaning in a composition of the present invention.

These various instruments, devices and equipment include, but are not limited to: diagnostic instruments, trays, pans, holders, racks, forceps, scissors, shears, saws (e.g. bone saws and

5 their blades), hemostats, knives, chisels, rongeurs, files, nippers, drills, drill bits, rasps, burrs, spreaders, breakers, elevators, clamps, needle holders, carriers, clips, hooks, gouges, curettes, retractors, straightener, punches, extractors, scoops, keratomes, spatulas, expressors, trocars, dilators, cages, glassware, tubing, catheters, cannulas, plugs, stents, arthoscopes and related equipment, and the like, or combinations thereof.

10 As used herein, "agricultural" or "veterinary" objects or surfaces include animal feeds, animal watering stations and enclosures, animal quarters, animal veterinarian clinics (e.g. surgical or treatment areas), animal surgical areas, and the like.

As used herein, weight percent (wt-%), percent by weight, % by weight, and the like are synonyms that refer to the concentration of a substance as the weight of that substance divided by the weight of the composition and multiplied by 100.

15 As used herein, the terms "mixed" or "mixture" when used relating to "peroxycarboxylic acid composition" or "peroxycarboxylic acids" refer to a composition or mixture including more than one peroxycarboxylic acid, such as a composition or mixture including peroxyacetic acid and peroxyoctanoic acid.

20 As used herein, the term "about" modifying the quantity of an ingredient in the compositions of the invention or employed in the methods of the invention refers to variation in the numerical quantity that can occur, for example, through typical measuring and liquid handling procedures used for making concentrates or use solutions in the real world; through inadvertent error in these procedures; through differences in the manufacture, source, or

25 purity of the ingredients employed to make the compositions or carry out the methods; and the like. The term about also encompasses amounts that differ due to different equilibrium conditions for a composition resulting from a particular initial mixture. Whether or not modified by the term "about", the claims include equivalents to the quantities.

Differentiation of antimicrobial "-cidal" or "-static" activity, the definitions which 30 describe the degree of efficacy, and the official laboratory protocols for measuring this efficacy are considerations for understanding the relevance of antimicrobial agents and

compositions. Antimicrobial compositions can effect two kinds of microbial cell damage. The first is a lethal, irreversible action resulting in complete microbial cell destruction or incapacitation. The second type of cell damage is reversible, such that if the organism is rendered free of the agent, it can again multiply. The former is termed bacteriocidal and the later, bacteriostatic. A sanitizer and a disinfectant are, by definition, agents which provide antibacterial or bacteriocidal activity. In contrast, a preservative is generally described as an inhibitor or bacteriostatic composition.

For the purpose of this patent application, successful reduction of microorganisms is achieved when the populations of microorganisms are reduced by at least about $0.3\text{-}1 \log_{10}$.

- 10 In this application, such a population reduction is the minimum acceptable for the processes. Any increased reduction in population of microorganisms is an added benefit that provides higher levels of protection.

Stabilized Ester Peroxycarboxylic Acid Compositions

15 The present invention relates to stabilized compositions containing an ester peroxydicarboxylic acid. Typically, the stabilized compositions also include a C₂ or higher alcohol. Typically, the ester peroxydicarboxylic acid is an antimicrobial agent. Ester peroxydicarboxylic acids undergo unacceptable degradation upon storage under conditions suitable for their synthesis and shipping, particularly in the presence of water.

20 Surprisingly, such unacceptable degradation can be slowed or halted by adding a C₂ or higher alcohol to the ester peroxydicarboxylic acid. The ester peroxydicarboxylic acid can be made in the presence of the C₂ or higher alcohol, or the C₂ or higher alcohol can be added after forming the ester peroxydicarboxylic acid. A preferred C₂ or higher alcohol can be employed in food products or for cleaning or sanitizing food processing equipment or materials. A preferred C₂ or higher alcohol can be employed in a health-care environment. A preferred C₂ or higher alcohol is non-toxic. A preferred C₂ or higher alcohol can be employed according to guidelines from government agencies, such as the Food and Drug Administration, without adverse labeling requirements, such as labeling with a skull and cross bones or the like. A preferred C₂ or higher alcohol is less toxic than methanol.

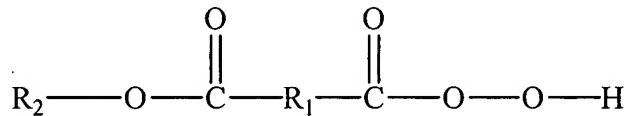
25 Preferred C₂ or higher alcohols include alcohols with about 2 to about 12 carbon atoms; C₂ or higher monohydric and polyhydric alcohols; glycols, glycerin, or phenols; and the like.

The C₂ or higher alcohol is typically present in a quantity that effectively stabilizes the ester peroxy carboxylic acid. Suitable levels of C₂ or higher alcohol include about 0.5 to about 80 wt-% C₂ or higher alcohol or about 1 to about 80 wt-% C₂ or higher alcohol, preferably about 0.5 to about 30 wt-% C₂ or higher alcohol or about 2 to about 30 wt-% C₂ or higher alcohol, and more preferably about 2 to about 15 wt-% C₂ or higher alcohol or about 4 to about 15 wt-% C₂ or higher alcohol.

Examples of suitable C₂ or higher alcohols include ethanol, n-propanol, isopropanol, n-butanol, isobutanol, tert-butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, glycerine, benzyl alcohol, cinnamyl alcohol, propylene glycol, butylene glycol, hexylene glycol, polyethylene glycol, polypropylene glycol, polybutylene glycol, and the like.

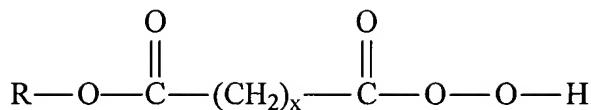
Preferred C₂ or higher alcohol s include ethanol, n-propanol, isopropanol, isobutanol, octanol, glycerine, propylene glycol, butylene glycol, hexylene glycol, polyethylene glycol, polypropylene glycol, polybutylene glycol, and the like. Preferred levels of ethanol include about 1 to about 40 wt-% ethanol, preferably about 2 to about 15 wt-% ethanol, and more preferably about 4 to about 10 wt-%. Preferred levels of isobutanol include about 1 to about 20 wt-% isobutanol, preferably about 2 to about 15 wt-% isobutanol, and most preferably about 3 to about 12 wt-% isobutanol.

As used herein, ester peroxy carboxylic acid refers to a molecule having the formula:



In this formula, R₁ and R₂ can independently be any of a wide variety of organic groups (e.g. alkyl, linear or cyclic, aromatic or saturated) or substituted organic groups (e.g., with one or more heteroatoms or organic groups). Ester peroxy carboxylic acid can be made using methods typically employed for producing peroxy carboxylic acid, such as incubating the corresponding ester carboxylic acid with hydrogen peroxide.

Preferred ester peroxy carboxylic acids include alkyl ester peroxy carboxylic acids, preferably having the formula:



where R represents an alkyl group having from 1 to 4 carbons and x is 0 to 5, preferably 1 to 4. The alkyl group can be either straight chain or branched. Preferably, R is a methyl, ethyl, 5 propyl, or isobutyl group. Preferably, x is 2, 3, or 4.

In one preferred embodiment, the composition of the present invention includes a mixture of alkyl ester peroxycarboxylic acids in which x is 2, 3, and 4. Such a mixture includes monoesters of peroxyadipic, peroxyglutaric, and peroxysuccinic acids. In another preferred embodiment, a majority of the ester peroxycarboxylic acid in the composition has x 10 equal to 3. In a preferred embodiment, R is a C₁-C₄ alkyl. In a preferred embodiment, x is 1, 2, 3, or 4. Most preferably, R is a C₁ alkyl, C₃ alkyl, or C₄ alkyl, and x is 2, 3 or 4.

In another preferred embodiment, R represents an alkyl group having from 1 to 8 carbons, and x is 0 to 10. The alkyl group can be either straight chain or branched, preferably straight chain. In this embodiment, preferably x is 4-8 and R is C₁ to C₄ alkyl, 15 preferably methyl or ethyl.

Alkyl ester peroxycarboxylic acids useful in this invention include monomethyl monoperoxyoxalic acid, monomethyl monoperoxymalonic acid, monomethyl monoperoxysuccinic acid, monomethyl monoperoxyglutaric acid, monomethyl monoperoxyadipic acid, monomethyl monoperoxypimelic acid, monomethyl monoperoxyisobutyric acid, and monomethyl monoperoxysebacic acid; monoethyl monoperoxyoxalic acid, monoethyl monoperoxymalonic acid, monoethyl monoperoxysuccinic acid, monoethyl monoperoxyglutaric acid, monoethyl monoperoxyadipic acid, monoethyl monoperoxypimelic acid, monoethyl monoperoxyisobutyric acid, and monoethyl monoperoxysebacic acid; monopropyl monoperoxyoxalic acid, 20 monopropyl monoperoxymalonic acid, monopropyl monoperoxysuccinic acid, monopropyl monoperoxyglutaric acid, monopropyl monoperoxyadipic acid, monopropyl monoperoxypimelic acid, monopropyl monoperoxyisobutyric acid, and monopropyl monoperoxysebacic acid, in which propyl can be n- or isopropyl; and monobutyl monoperoxyoxalic acid, monobutyl monoperoxymalonic acid, monobutyl monoperoxysuccinic acid, monobutyl 25 monoperoxyglutaric acid, monobutyl monoperoxyadipic acid, monobutyl monoperoxypimelic acid, monobutyl monoperoxyisobutyric acid, and monobutyl monoperoxysebacic acid, in which butyl can be n- or isobutyl.

monoperoxyadipic acid, monobutyl monoperoxy-pimelic acid, monobutyl monoperoxy-suberic acid, and monobutyl monoperoxysebacic acid, in which butyl can be n-, iso-, or t-butyl.

Stabilized compositions of ester peroxy-carboxylic acid can also include other ingredients, for example, to increase solubility of the ester peroxy-carboxylic acid or to maintain the pH of the composition. Preferably the stabilized composition includes a surfactant. It is believed that the surfactant can increase the solubility of the ester peroxy-carboxylic acid. Suitable surfactants include nonionic surfactants, anionic surfactants, cationic surfactants, amphoteric surfactants, and the like. Preferred surfactants include alkylbenzene sulfonic acids and their salts, alkyl sulfonates, straight-chain or branched alcohol ethoxylates, amine oxides, and the like. Preferably the surfactant is present at about 0 to about 15 wt-% of the composition, preferably about 0 to about 10 wt-%, and most preferably about 0 to about 8 wt-%.

Preferably the stabilized composition includes a buffer. Preferred buffers maintain the pH of the composition, after dilution to the use concentration, below about 7, preferably below about 5, and more preferably below about 4. Preferred buffers include citric acid and its salts, phosphoric acid and its salts, succinic acid and its salts, adipic acid and its salts, glutaric acid and its salts, acetic acid and its salts, boric acid and its salts, and mixtures thereof. Preferably the buffer is present at about 0 to about 20 wt-% of the composition, preferably about 0 to about 10 wt-%, and most preferably about 0 to about 7 wt-%.

Preferably, the stabilized ester peroxy-carboxylic acid composition maintains suitable levels of the ester peroxy-carboxylic acid, or a stable trans-esterified derivative, in the composition. Preferably, the amount or concentration of ester peroxy-carboxylic acid remains at more than about 50 wt-% for at least about 3 months, preferably at more than about 70 wt-%, and most preferably at more than about 85 wt-%.

Preferably, the stabilized ester peroxy-carboxylic acid retains antimicrobial activity. Preferably, upon formulating with C₂ or higher alcohol according to the invention, the ester peroxy-carboxylic acid composition retains at least about 30 % of its antimicrobial activity for at least about 3 months, preferably at more than about 50 %, and most preferably at more than about 70 %.

The stabilized compositions of the invention can be formulated as a liquid, a gel, an aerosol, a gas, a wax, a solid, or a powder, or as a solution or suspension containing such a composition.

5 **Peroxycarboxylic Acid Antimicrobial Compositions**

Compositions of Carboxylic Acids and Peroxycarboxylic Acids

Among other constituents, the composition of the present invention includes a carboxylic acid. Generally, carboxylic acids have the formula R-COOH wherein the R can represent any number of different groups including aliphatic groups, alicyclic groups, aromatic groups, heterocyclic groups, and ester groups, such as alkyl ester groups, all of which can be saturated or unsaturated and/or substituted or unsubstituted. Carboxylic acids can have one, two, three, or more carboxyl groups. Preferred ester groups include aliphatic ester groups, such as R₁OC(O)R₂- where each of R₁ and R₂ can be aliphatic, preferably alkyl, groups described above for R. Preferably R₁ and R₂ are each independently small alkyl groups, such as alkyl groups with 1 to 4 carbon atoms.

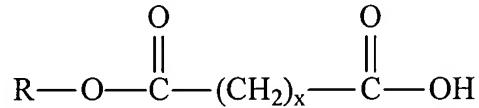
The composition and methods of the invention can employ carboxylic acids containing as many as 18 carbon atoms. Examples of suitable carboxylic acids include formic, acetic, propionic, butanoic, pentanoic, hexanoic, heptanoic, octanoic, nonanoic, decanoic, undecanoic, dodecanoic, lactic, maleic, ascorbic, citric, hydroxyacetic (glycolic), neopentanoic, neoheptanoic, neodecanoic, oxalic, malonic, succinic, glutaric, adipic, pimelic suberic, and sebacic acid. Examples of suitable alkyl ester carboxylic acids include monomethyl oxalic acid, monomethyl malonic acid, monomethyl succinic acid, monomethyl glutaric acid, monomethyl adipic acid, monomethyl pimelic acid, monomethyl suberic acid, and monomethyl sebacic acid; monoethyl oxalic acid, monoethyl malonic acid, monoethyl succinic acid, monoethyl glutaric acid, monoethyl adipic acid, monoethyl pimelic acid, monoethyl suberic acid, and monoethyl sebacic acid; monopropyl oxalic acid, monopropyl malonic acid, monopropyl succinic acid, monopropyl glutaric acid, monopropyl adipic acid, monopropyl pimelic acid, monopropyl suberic acid, and monopropyl sebacic acid, in which propyl can be n- or isopropyl; and monobutyl oxalic acid, monobutyl malonic acid, monobutyl succinic acid, monobutyl glutaric acid, monobutyl adipic acid, monobutyl pimelic

acid, monobutyl suberic acid, and monobutyl sebacic acid, in which butyl can be n-, iso-, or t-butyl.

Carboxylic acids which are generally useful are those having one or two carboxyl groups where the R group is a primary alkyl chain having a length of C₂ to C₁₂. The primary alkyl chain is that carbon chain of the molecule having the greatest length of carbon atoms and directly appending carboxyl functional groups. Longer chain carboxylic acid analogues, including hexanoic, heptanoic, octanoic, nonanoic, and decanoic, can reduce surface tension to assist in wetting of hydrophobic surfaces like skin.

In a preferred embodiment, the antimicrobial composition includes one or more mono- or di-carboxylic acids having up to 18 carbon atoms. Preferred mono- or di-carboxylic acids having up to 18 carbon atoms include acetic acid, lactic acid, glycolic acid, citric acid, heptanoic acid, octanoic acid, nonanoic acid, or a mixture thereof. In another preferred embodiment, the antimicrobial composition includes an alpha-hydroxy mono- or di-carboxylic acid having from 3 to 6 carbon atoms, preferably lactic acid.

Carboxylic acids that are generally useful include ester carboxylic acids, such as alkyl ester carboxylic acids. Preferred alkyl ester carboxylic acids include those with the formula:



where R represents an alkyl group having from 1 to 4 carbons and x is 0 to 5, preferably 1 to 4. The alkyl group can be either straight chain or branched. Preferably, R is a methyl, ethyl, propyl, or isobutyl group. Preferably, x is 2, 3, or 4.

In one preferred embodiment, the composition of the present invention includes a mixture of alkyl ester peroxycarboxylic acids in which x is 2, 3, and 4. Such a mixture includes monoesters of peroxyadipic, peroxyglutaric, and peroxysuccinic acids. In another preferred embodiment, a majority of the ester peroxycarboxylic acid in the composition has x equal to 3. In a preferred embodiment, R is a C₁-C₄ alkyl. In a preferred embodiment, x is 1, 2, 3, or 4. Most preferably, R is a C₁ alkyl, C₃ alkyl, or C₄ alkyl, and x is 2, 3 or 4.

In another preferred embodiment, R represents an alkyl group having from 1 to 8 carbons, and x is 0 to 10. The alkyl group can be either straight chain or branched,

preferably straight chain. In this embodiment, preferably x is 4-8 and R is C₁ to C₄ alkyl, preferably methyl or ethyl.

Generally, the concentration of carboxylic acid within the composition used in the process of the invention ranges from about 0.5 wt-% to about 80 wt-%, preferably from about 5 wt-% to about 50 wt-%, and most preferably from about 10 wt-% to about 30 wt-%.

Typically the concentration of ester carboxylic acid ranges up to about 15% by weight, although concentrations of up to 50% can be employed in certain embodiments, preferably from about 0.05 to about 15%, and most preferably from about 1% to about 9%.

Peroxycarboxylic (or percarboxylic) acids generally have the formula R(CO₃H)_n, where R is an alkyl, arylalkyl, cycloalkyl, aromatic, heterocyclic, or ester group, such as an alkyl ester group; and n is one, two, or three, and named by prefixing the parent acid with peroxy. Ester groups are defined as R groups including organic moieties (such as those listed above for R) and ester moieties. Preferred ester groups include aliphatic ester groups, such as R₁OC(O)R₂- where each of R₁ and R₂ can be aliphatic, preferably alkyl, groups described above for R. Preferably R₁ and R₂ are each independently small alkyl groups, such as alkyl groups with 1 to 5 carbon atoms.

While peroxycarboxylic acids are not as stable as carboxylic acids, their stability generally increases with increasing molecular weight. Thermal decomposition of these acids can generally proceed by free radical and nonradical paths, by photodecomposition or radical-induced decomposition, or by the action of metal ions or complexes. Percarboxylic acids can be made by the direct, acid catalyzed equilibrium action of hydrogen peroxide with the carboxylic acid, by autoxidation of aldehydes, or from acid chlorides, and hydrides, or carboxylic anhydrides with hydrogen or sodium peroxide.

Peroxycarboxylic acids useful in the compositions and methods of the present invention include peroxyformic, peroxyacetic, peroxypropionic, peroxybutanoic, peroxypentanoic, peroxyhexanoic, peroxyheptanoic, peroxyoctanoic, peroxynonanoic, peroxydecanoic, peroxyundecanoic, peroxydodecanoic, peroxylactic, peroxycitric, peroxymaleic, peroxyascorbic, peroxyhydroxyacetic (peroxyglycolic), peroxyoxalic, peroxymalonic, peroxysuccinic, peroxyglutaric, peroxyadipic, peroxytrimelic, peroxyisobutyric, and peroxysebacic acid, and mixtures thereof. Useful peroxycarboxylic acids also include

the ester peroxydicarboxylic acids described herein above and compositions of the present invention including those ester peroxydicarboxylic acids.

Peroxy forms of carboxylic acids with more than one carboxylate moiety can have one or more of the carboxyl moieties present as peroxy carboxyl moieties. These peroxy carboxylic acids have been found to provide good antimicrobial action with good stability in aqueous mixtures. In a preferred embodiment, the composition of the invention utilizes a combination of several different peroxy carboxylic acids.

In a preferred embodiment, the composition of the invention utilizes a combination of several different peroxy carboxylic acids. Preferably, the composition includes one or more small C₂-C₄ peroxy carboxylic acids, one or more large C₈-C₁₂ peroxy carboxylic acids, and/or one or more alkyl ester peroxy carboxylic acid compositions. Especially preferred is an embodiment in which the small peroxy carboxylic acid is peroxyacetic acid and the large acid is either peroxyoctanoic acid or peroxydecanoic acid.

In a preferred embodiment, the antimicrobial composition includes one or more alkyl ester peroxy carboxylic acids and a peroxy carboxylic acid having from 2 to 12 carbon atoms. Preferably, such an antimicrobial composition includes peroxyacetic acid, or peroxyoctanoic acid, or peroxydecanoic acid, and monomethyl monoperoxyoxalic acid, monomethyl monoperoxymalonic acid, monomethyl monoperoxy succinic acid, monomethyl monoperoxyglutaric acid, monomethyl monoperoxy adipic acid, monomethyl monoperoxy pimelic acid, monomethyl monoperoxy suberic acid, or monomethyl monoperoxy sebacic acid; monoethyl monoperoxyoxalic acid, monoethyl monoperoxymalonic acid, monoethyl monoperoxy succinic acid, monoethyl monoperoxyglutaric acid, monoethyl monoperoxy adipic acid, monoethyl monoperoxy pimelic acid, monoethyl monoperoxy suberic acid, or monoethyl monoperoxy sebacic acid; monopropyl monoperoxyoxalic acid, monopropyl monoperoxymalonic acid, monopropyl monoperoxy succinic acid, monopropyl monoperoxyglutaric acid, monopropyl monoperoxy adipic acid, monopropyl monoperoxy pimelic acid, monopropyl monoperoxy suberic acid, or monopropyl monoperoxy sebacic acid, in which propyl can be n- or isopropyl; or monobutyl monoperoxyoxalic acid, monobutyl monoperoxymalonic acid, monobutyl monoperoxy succinic acid, monobutyl monoperoxyglutaric acid, monobutyl

monoperoxyadipic acid, monobutyl monoperoxy-pimelic acid, monobutyl monoperoxy-suberic acid, or monobutyl monoperoxysebacic acid, in which butyl can be n-, iso-, or t-butyl, or mixtures thereof. Preferably, in such mixtures the alkyl ester peroxy-carboxylic acids is one of the above, and the peroxy-carboxylic acid having from 2 to 12 carbon atoms is

5 peroxyacetic acid or peroxyoctanoic acid; combined in a ratio of about 1 to about 10 parts by weight of peroxyacetic acid per each 1 part of carboxylic acid. In another embodiment, when a blended acid is used, the peroxy-carboxylic acids are blended in proportions that range from about 1 part to about 20 parts by weight of alkyl ester peroxyacid to mono- or di-peroxy-carboxylic acid having up to 12 carbon atoms. In another preferred embodiment, the

10 combination of peroxy-carboxylic acid includes an alkyl ester peroxyacid and a mono- or di-peroxy-carboxylic acid having up to 12 carbon atoms.

The amount of alkyl ester peroxy-carboxylic acid in use and concentrate compositions can range up to the limits at which the peroxy-carboxylic acid can be dissolved or suspended in the composition. Preferably, the alkyl ester peroxy-carboxylic acid is present in a use or concentrate composition at a concentration of from about 0.0001 to about 20% by weight, preferably from about 0.05 to about 15% by weight, and more preferably from about 4 to about 10% by weight. Typically use compositions include at least 0.1%, preferably at least 1%, by weight alkyl ester peroxy-carboxylic acid.

A preferred antimicrobial stabilized ester peroxy-carboxylic acid composition of the present invention is effective for killing one or more of the food-borne pathogenic bacteria associated with a food product, such as *Salmonella typhimurium*, *Salmonella javiana*, *Campylobacter jejuni*, *Listeria monocytogenes*, and *Escherichia coli* O157:H7, yeast, mold and the like. The compositions and methods of the present invention have activity against a wide variety of microorganisms such as Gram positive (for example, *Listeria monocytogenes*) and Gram negative (for example, *Escherichia coli*) bacteria, yeast, molds, bacterial spores, viruses, etc. The compositions and methods of the present invention, as described above, have activity against a wide variety of human pathogens. The compositions and methods can kill a wide variety of microorganisms on a food processing surface, on the surface of a food product, or in water used for washing or processing of food product.

30 A preferred antimicrobial stabilized ester peroxy-carboxylic acid composition of the present invention is effective for killing one or more of the pathogenic bacteria associated

with a health care surfaces and environments, such as *Salmonella typhimurium*, *Staphylococcus aureus*, *Salmonella choleraesurus*, *Pseudomonas aeruginosa*, and *Escherichia coli*, mycobacteria, yeast, mold, and the like. The compositions and methods of the present invention have activity against a wide variety of microorganisms such as Gram positive (for example, *Staphylococcus aureus*) and Gram negative (for example, *Pseudomonas aeruginosa*) bacteria, yeast, molds, bacterial spores, viruses, etc. The compositions and methods of the present invention, as described above, have activity against a wide variety of human pathogens. The compositions and methods can kill a wide variety of microorganisms on a health care surface or in a health care environment.

10 The preferred compositions include concentrate compositions and use compositions. Typically, an antimicrobial concentrate composition can be diluted, for example with water, to form an antimicrobial use composition. In a preferred embodiment, the concentrate composition is diluted into water employed for washing or processing food product.

15 The advantageous stability of mixed peroxyacidic acid compositions in such methods, which include the presence of food product or health care debris or residue, makes these compositions competitive with cheaper, less stable, and potentially toxic chlorinated compounds. Preferred methods of the present invention include agitation or sonication of the use composition, particularly as a concentrate is added to water to make the use composition. Preferred methods include water systems that have some agitation, spraying, or other mixing of the solution.

20 The level of reactive species, such as peroxy acids and/or hydrogen peroxide, in a use composition can be affected, typically diminished, by organic matter that is found in or added to the use composition. For example, when the use composition is a bath or spray used for washing food product, food product organic matter or accompanying organic matter will consume peroxy acid and peroxide. Thus, the amounts of ingredients listed for the use compositions refer to the composition before or early in use, with the understanding that the amounts will diminish as organic matter is added to the use composition.

25 In addition, the concentrate and use compositions change with age. It is believed that in approximately one year at ambient conditions the amount of peroxyacidic acid in the compositions can decrease to about 50% to about 80%, preferably about 80% to about 85%,

of the initial equilibrium values or use composition levels. Such aged compositions are included in the scope of the present invention.

In an embodiment, the compositions of the present invention preferably include only ingredients that can be employed in food products or in food product washing, handling, or processing, for example, according to government (e.g., FDA or USDA) rules and regulations. Preferably, the composition is free of any non-ester peroxyacidic acid or carboxylic acid with 10, 12, or more carbon atoms. Such non-ester 10, 12, or more carbon acids can impart undesirable residues (e.g., bad tasting and/or malodorous) to food product.

Each of the compositions listed above can be formulated by combining each of the listed ingredients. In addition, certain compositions including both acid and peroxy acid can be formulated by combining the acids and hydrogen peroxide, which forms peroxy acids. Typically, the pH of an equilibrium mixture is less than about 1 or about 2, and the pH of a 1% solution of the equilibrium mixture in water is about 2 to about 7, depending on the other components of the 1% solution, and the pH of a use composition can be from about 3 to about 7 depending on the other components.

Hydrogen Peroxide

The stabilized compositions of the invention typically also include a hydrogen peroxide constituent. Hydrogen peroxide in combination with the percarboxylic acid provides certain antimicrobial action against microorganisms. Additionally, hydrogen peroxide can provide an effervescent action which can irrigate any surface to which it is applied. Hydrogen peroxide works with a mechanical flushing action once applied which further cleans the surface. An additional advantage of hydrogen peroxide is the food compatibility of this composition upon use and decomposition. For example, combinations of peroxyacetic acid, peroxyoctanoic acid, and hydrogen peroxide result in acetic acid, octanoic acid, water, and oxygen upon decomposition, all of which are food product compatible.

Many oxidizing agents can be used for generating peroxyacidic acids. Suitable oxidizing agents, in addition to hydrogen peroxide, include salts of perborate, percarbonate, and persulfate. Hydrogen peroxide is generally preferred for several reasons. After application of the H₂O₂/peroxyacidic acid germicidal agent, the residue left merely

includes water and an acidic constituent. Deposition of these products on the surface of a food product processing apparatus, such as a bath or spray apparatus, will not adversely effect the apparatus, the handling or processing, or the food product washed therein.

Hydrogen peroxide (H_2O_2), has a molecular weight of 34.014 and it is a weakly
5 acidic, clear, colorless liquid. The four atoms are covalently bonded in a H-O-O-H structure. Generally, hydrogen peroxide has a melting point of -0.41 °C, a boiling point of 150.2 °C, a density at 25 °C of 1.4425 grams per cm³, and a viscosity of 1.245 centipoise at 20 °C.

Carrier

10 The stabilized composition of or employed in the method of the invention also includes a carrier. The carrier provides a medium which dissolves, suspends, or carries the other components of the stabilized composition. For example, the carrier can provide a medium for solubilization and production of peroxy carboxylic acid and for forming an equilibrium mixture. The carrier also functions to deliver and wet the stabilized composition of the invention to the food product. To this end, the carrier may contain any component or components that can facilitate these functions.
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Polyols are also useful carriers, including polypropylene glycols, polyethylene
20 glycols, sorbitol, and the like. Any of these compounds may be used singly or in combination with other organic or inorganic constituents or, in combination with water or in mixtures thereof.

Generally, the carrier makes up a large portion of the composition and may be the balance of the composition apart from the active antimicrobial components, adjuvants, and the like. Here again, the carrier concentration and type will depend upon the nature of the composition as a whole, the environmental storage, and method of application including
25 concentration of the antimicrobial agent, among other factors. Notably the carrier should be chosen and used at a concentration which does not inhibit the antimicrobial efficacy of the active agent in the composition.

Adjuvants

30 The stabilized composition of or employed in the method of the invention can also include any number of adjuvants. Specifically, the composition can include stabilizing

agents, wetting agents, hydrotropes, thickeners, a surfactant, foaming agents, acidifiers, as well as pigments or dyes among any number of constituents which can be added to the composition. Such adjuvants can be preformulated with the stabilized composition or added to the system simultaneously, or even after, the addition of the stabilized composition. The 5 composition can also contain any number of other constituents as necessitated by the application, which are known to those of skill in the art and which can facilitate the activity of the present invention.

Stabilizing Agents

10 Stabilizing agents can be added to the composition, for example, to stabilize the peracid and hydrogen peroxide and prevent the premature oxidation of this constituent within the composition.

Chelating agents or sequestrants generally useful as stabilizing agents in the present compositions include alkyl diamine polyacetic acid-type chelating agents such as EDTA (ethylene diamine tetraacetate tetrasodium salt), acrylic and polyacrylic acid-type stabilizing agents, phosphonic acid, and phosphonate-type chelating agents among others. Preferable sequestrants include phosphonic acids and phosphonate salts including 1-hydroxy ethyldene-1,1-diphosphonic acid ($\text{CH}_3\text{C}(\text{PO}_3\text{H}_2)_2\text{OH}$) (HEDP), amino[tri(methylene phosphonic acid)] ($[\text{CH}_2\text{PO}_3\text{H}_2]_2$ (ethylene diamine[tetra methylene-phosphonic acid])], 2-phosphene butane-1,2,4-tricarboxylic acid, as well as the alkyl metal salts, ammonium salts, or alkyloyl amine salts, such as mono, di, or tetra-ethanolamine salts. The stabilizing agent is used in a concentration ranging from about 0 weight percent to about 20 weight percent of the composition, preferably from about 0.1 weight percent to about 10 weight percent of the composition, and most preferably from about 0.2 weight percent to 5 weight percent of the 20 composition.
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Amino phosphates and phosphonates are also suitable for use as chelating agents in the compositions and include ethylene diamine (tetramethylene phosphonates), nitrilotrismethylene phosphates, diethylenetriamine (pentamethylene phosphonates). These amino phosphonates commonly contain alkyl or alkaline groups with less than 8 carbon atoms. The phosphonic acid may also include a low molecular weight phosphonopolycarboxylic acid such as one having about 2-4 carboxylic acid moieties and
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about 1-3 phosphonic acid groups. Such acids include 1-phosphono-1-methylsuccinic acid, phosphonosuccinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid.

Commercially available food additive chelating agents include phosphonates sold under the trade name DEQUEST® including, for example, 1-hydroxyethyldene-1,1-diphosphonic acid, available from Monsanto Industrial Chemicals Co., St. Louis, MO, as DEQUEST® 2010; amino(tri(methylenephosphonic acid)), ($N[CH_2PO_3H_2]_3$), available from Monsanto as DEQUEST® 2000; ethylenediamine[tetra(methylenephosphonic acid)] available from Monsanto as DEQUEST® 2041; and 2-phosphonobutane-1,2,4-tricarboxylic acid available from Mobay Chemical Corporation, Inorganic Chemicals Division, Pittsburgh, PA, as Bayhibit AM.

The above-mentioned phosphonic acids can also be used in the form of water soluble acid salts, particularly the alkali metal salts, such as sodium or potassium; the ammonium salts or the alkylol amine salts where the alkylol has 2 to 3 carbon atoms, such as mono-, di-, or triethanolamine salts. If desired, mixtures of the individual phosphonic acids or their acid salts can also be used.

The concentration of chelating agent useful in the present invention generally ranges from about 0.01 to about 10 wt-%, preferably from about 0.1 to about 5 wt-%, most preferably from about 0.5 to about 2 wt-%.

20 Wetting or Defoaming Agents

Also useful in the composition are wetting and defoaming agents. Wetting agents function to increase the surface contact or penetration activity of the stabilized composition. Wetting agents which can be used in the composition include any of those constituents known within the art to raise the surface activity of the composition.

Along these lines, surfactants, and especially nonionic surfactants, can also be useful in the present invention. Nonionic surfactants which can be useful in the present invention are those which include ethylene oxide moieties, propylene oxide moieties, as well mixtures thereof, and ethylene oxide-propylene oxide moieties in either heteric or block formation. Additionally useful in the present invention are nonionic surfactants which include an alkyl ethylene oxide compounds, alkyl propylene oxide compounds, as well as mixtures thereof, and alkyl ethylene oxide-propylene oxide compounds where the ethylene oxide propylene

oxide moiety is either in heteric or block formation. Further useful in the present invention are nonionic surfactants having any mixture or combination of ethylene oxide-propylene oxide moieties linked to a alkyl chain where the ethylene oxide and propylene oxide moieties can be in any randomized or ordered pattern and of any specific length. Nonionic surfactants 5 useful in the present invention can also include randomized sections of block and heteric ethylene oxide propylene oxide, or ethylene oxide-propylene oxide, such as ethylene diamine ethylene oxides, ethylene diamine propylene oxides, mixtures thereof, and ethylene diamine EO-PO compounds, including those sold under the tradename Tetronic.

Generally, the concentration of nonionic surfactant used in a composition of the 10 present invention can range from about 0 wt-% to about 5 wt-% of the composition, preferably from about 0 wt-% to about 2 wt-% of the concentrate composition, and most preferably from about 0 wt-% to about 1 wt-% of the composition.

The composition can also contain additional ingredients as necessary to assist in defoaming. Generally, defoamers which can be used in accordance with the invention 15 include silica and silicones; aliphatic acids or esters; alcohols; sulfates or sulfonates; amines or amides; halogenated compounds such as fluorochlorohydrocarbons; vegetable oils, waxes, mineral oils as well as their sulfated derivatives; fatty acid soaps such as alkali, alkaline earth metal soaps; and phosphates and phosphate esters such as alkyl and alkaline diphosphates, and tributyl phosphates among others; and mixtures thereof.

Especially preferably, are those antifoaming agents or defoamers which are of food 20 grade quality given the application of the method of the invention. To this end, one of the more effective antifoaming agents includes silicones. Silicones such as dimethyl silicone, glycol polysiloxane, methylphenol polysiloxane, trialkyl or tetraalkyl silanes, hydrophobic silica defoamers and mixtures thereof can all be used in defoaming applications.

Commercial defoamers commonly available include silicones such as Ardefoam® from 25 Armour Industrial Chemical Company which is a silicone bound in an organic emulsion; Foam Kill® or Kresseo® available from Krusble Chemical Company which are silicone and non-silicone type defoamers as well as silicone esters; and Anti-Foam A® and DC-200 from Dow Corning Corporation which are both food grade type silicones among others.

These defoamers can be present at a concentration range from about 0.01 wt-% to 5 wt-%, 30

preferably from about 0.01 wt-% to 2 wt-%, and most preferably from about 0.01 wt-% to about 1 wt-%.

Hydrotrope

5 The food product wash composition of the invention or employed in the method of the invention can also include a hydrotrope coupler or solubilizer. Such materials can be used to ensure that the composition remains phase stable and in a single highly active aqueous form. Such hydrotrope solubilizers or couplers can be used at concentrations that maintain phase stability but do not result in unwanted compositional interaction.

10 Representative classes of hydrotrope solubilizers or coupling agents include an anionic surfactant such as an alkyl sulfate, an alkyl or alkane sulfonate, a linear alkyl benzene or naphthalene sulfonate, a secondary alkane sulfonate, alkyl ether sulfate or sulfonate, an alkyl phosphate or phosphonate, dialkyl sulfosuccinic acid ester, sugar esters (e.g., sorbitan esters) and a C₈₋₁₀ alkyl glucoside.

15 Preferred coupling agents for use in the present compositions and methods include n-octane sulfonate and aromatic sulfonates such as an alkyl aryl sulfonate (e.g., sodium xylene sulfonate or naphthalene sulfonate). Many hydrotrope solubilizers independently exhibit some degree of antimicrobial activity at low pH. Such action adds to the efficacy of the invention but is not a primary criterion used in selecting an appropriate solubilizing agent.

20 Since the presence of the peroxy carboxylic acid material in the protonated neutral state provides beneficial biocidal or antimicrobial activity, the coupling agent should be selected not for its independent antimicrobial activity but for its ability to provide effective single phase composition stability in the presence of substantially insoluble peroxy carboxylic acid materials and the more soluble compositions of the invention. Generally, any number of surfactants may be used consistent with the purpose of this constituent.

25 Anionic surfactants useful with the invention include alkyl carboxylates, linear alkylbenzene sulfonates, paraffin sulfonates and secondary n-alkane sulfonates, sulfosuccinate esters and sulfated linear alcohols.

30 Zwitterionic or amphoteric surfactants useful with the invention include β-N-alkylaminopropionic acids, n-alkyl-β-iminodipropionic acids, imidazoline carboxylates, n-alky-Iletaines, amine oxides, sulfobetaines and sultaines.

Nonionic surfactants useful in the context of this invention are generally polyether (also known as polyalkylene oxide, polyoxyalkylene or polyalkylene glycol) compounds. More particularly, the polyether compounds are generally polyoxypropylene or polyoxyethylene glycol compounds. Typically, the surfactants useful in the context of this
5 invention are synthetic organic polyoxypropylene (PO)-polyoxyethylene (EO) block copolymers. These surfactants have a diblock polymer including an EO block and a PO block, a center block of polyoxypropylene units (PO), and having blocks of polyoxyethylene grafted onto the polyoxypropylene unit or a center block of EO with attached PO blocks. Further, this surfactant can have further blocks of either polyoxyethylene or
10 polyoxypropylene in the molecule. The average molecular weight of useful surfactants ranges from about 1000 to about 40,000 and the weight percent content of ethylene oxide ranges from about 10-80% by weight.

Also useful in the context of this invention are surfactants including alcohol alkoxylates having EO, PO and BO blocks. Straight chain primary aliphatic alcohol alkoxylates can be particularly useful as sheeting agents. Such alkoxylates are also available from several sources including BASF Wyandotte where they are known as "Plurafac" surfactants. A particular group of alcohol alkoxylates found to be useful are those having the general formula R-(EO)_m-(PO)_n wherein m is an integer of about 2-10 and n is an integer from about 2-20. R can be any suitable radical such as a straight chain alkyl group having from about 6-20 carbon atoms.
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Other useful nonionic surfactants include capped aliphatic alcohol alkoxylates. These end caps include but are not limited to methyl, ethyl, propyl, butyl, benzyl and chlorine. Useful alcohol alkoxylated include ethylene diamine ethylene oxides, ethylene diamine propylene oxides, mixtures thereof, and ethylene diamine EO-PO compounds, including
25 those sold under the tradename Tetronic. Preferably, such surfactants have a molecular weight of about 400 to 10,000. Capping improves the compatibility between the nonionic and the oxidizers hydrogen peroxide and peroxyacrylic acid, when formulated into a single composition. Other useful nonionic surfactants are alkylpolyglycosides.

Another useful nonionic surfactant is a fatty acid alkoxylate wherein the surfactant includes a fatty acid moiety with an ester group including a block of EO, a block of PO or a mixed block or heteric group. The molecular weights of such surfactants range from about
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400 to about 10,000, a preferred surfactant has an EO content of about 30 to 50 wt-% and wherein the fatty acid moiety contains from about 8 to about 18 carbon atoms.

Similarly, alkyl phenol alkoxylates have also been found useful in the invention. Such surfactants can be made from an alkyl phenol moiety having an alkyl group with 4 to 5 about 18 carbon atoms, can contain an ethylene oxide block, a propylene oxide block or a mixed ethylene oxide, propylene oxide block or heteric polymer moiety. Preferably such surfactants have a molecular weight of about 400 to about 10,000 and have from about 5 to about 20 units of ethylene oxide, propylene oxide or mixtures thereof.

The concentration of hydrotrope useful in the present invention generally ranges from 10 about 0.1 to about 20 wt-%, preferably from about 0.5 to about 10 wt-%, most preferably from about 1 to about 4 wt-%.

Thickening or Gelling Agents

15 Thickeners useful in the present invention include those which do not leave contaminating residue on the surface of food product or food product processing apparatus. That is, preferred thickeners or gelling agents do not include components incompatible with food or other sensitive products in contact areas.

20 Generally, thickeners which may be used in the present invention include natural gums such as xanthan gum, guar gum, or other gums from plant mucilage; polysaccharide based thickeners, such as alginates, starches, and cellulosic polymers (e.g., carboxymethyl cellulose); polyacrylates thickeners; and hydrocolloid thickeners, such as pectin. Generally, the concentration of thickener employed in the present compositions or methods will be dictated by the desired viscosity within the final composition. However, as a general guideline, the viscosity of thickener within the present composition ranges from about 0.1 25 wt-% to about 1.5 wt-%, preferably from about 0.1 wt-% to about 1.0 wt-%, and most preferably from about 0.1 wt-% to about 0.5 wt-%.

Formulation

30 The compositions of or used in the methods of the invention can be formulated by combining the antimicrobially active materials (e.g., aliphatic carboxylic mono- or di-esters, and hydrogen peroxide) with adjuvant or other components with the materials that form the

stabilized composition. The compositions can also be formulated with preformed peroxydicarboxylic acids. The preferred compositions of the invention can be made by mixing the aliphatic carboxylic mono- or di-esters or mixture thereof with an optional hydrotrope solubilizer or coupler, reacting the mixture with hydrogen peroxide and then adding the balance of required ingredients to provide rinsing and antimicrobial action.

A stable equilibrium mixture is produced containing the carboxylic acid or blend with hydrogen peroxide and allowing the mixture to stand for 1-14 days at 15°C or more. With this preparatory method, an equilibrium mixture will be formed containing an amount of hydrogen peroxide, unoxidized acid, oxidized or peroxydicarboxylic acid and unmodified 10 couplers, solubilizer, or stabilizers.

Use Compositions

The invention contemplates a concentrate composition which is diluted to a use solution prior to application to an object. Primarily for reasons of economics, the concentrate would normally be marketed and an end user would preferably dilute the concentrate with water or an aqueous diluent to a use solution.

The level of active components in the concentrate composition is dependent on the intended dilution factor and the desired activity of the peroxydicarboxylic acid compound and the carboxylic acid. Generally, a dilution of about 0.5 to about 20 fluid ounces to about 100 gallons of water is used for aqueous antimicrobial compositions. Higher use dilutions can be employed if elevated use temperature (greater than 25 °C) or extended exposure time (greater than 30 seconds) can be employed. In the typical use locus, the concentrate is diluted with a major proportion of water using commonly available tap or service water mixing the materials at a dilution ratio of about 3 to about 20 ounces of concentrate per 100 gallons of water.

Methods Employing the Stabilized Ester Peroxydicarboxylic Acid Compositions

The present invention includes methods employing the stabilized ester peroxydicarboxylic acid compositions. Typically, these methods employ the antimicrobial or bleaching activity of the ester peroxydicarboxylic acid. For example, the invention includes a method for reducing a microbial population, a method for reducing the population of a

microorganism on skin, a method for treating a disease of skin, a method for reducing an odor, a method for bleaching. These methods can operate on an object, surface, in a body or stream of water or a gas, or the like, by contacting the object, surface, body, or stream with a stabilized ester peroxy carboxylic acid composition of the invention. Contacting can include
5 any of numerous methods for applying a composition, such as spraying the composition, immersing the object in the composition, foam or gel treating the object with the composition, or a combination thereof.

The present stabilized compositions can be employed for reducing the population of pathogenic microorganisms, such as pathogens of humans, animals, and the like. The

10 stabilized compositions can exhibit activity against pathogens including fungi, molds, bacteria, spores, and viruses, for example, parvovirus, coxsackie virus, herpes virus, *S. aureus*, *E. coli*, *Streptococci*, *Legionella*, mycobacteria, or the like. Such pathogens can cause a varieties of diseases and disorders, including athletes foot, hairy hoof wart disease, Mastitis or other mammalian milking diseases, tuberculosis, and the like. The compositions

15 of the present invention can reduce the population of microorganisms on skin or other external or mucosal surfaces of an animal. In addition, the present compositions can kill pathogenic microorganisms that spread through transfer by water, air, or a surface substrate.

The composition need only be applied to the skin, other external or mucosal surfaces of an animal water, air, or surface. A filter containing the composition can reduce the population
20 of microorganisms in air and liquids.

A concentrate or use concentration of a stabilized ester peroxy carboxylic acid composition of the present invention can be applied to or brought into contact with an object by any conventional method or apparatus for applying an antimicrobial or cleaning composition to an object. For example, the object can be wiped with, sprayed with, and/or
25 immersed in the stabilized composition, or a use composition made from the stabilized composition. Contacting can be manual or by machine. Food processing surfaces, food products, food processing or transport waters, and the like can be treated with liquid, gel, aerosol, gas, wax, solid, or powdered stabilized compositions according to the invention, or solutions containing these compositions.

Contacting a Food Product with the Stabilized Ester Peroxycarboxylic Acid Compositions

The present method and system provide for contacting a food product with a stabilized composition employing any method or apparatus suitable for applying a stabilized composition. For example, the method and system of the invention can contact the food product with a spray of a stabilized composition, by immersion in the stabilized composition, by foam or gel treating with the stabilized composition, or the like. Contact with a spray, a foam, a gel, or by immersion can be accomplished by a variety of methods known to those of skill in the art for applying antimicrobial agents to food. These same methods can also be adapted to apply the stabilized compositions of the invention to other objects.

10 The present methods require a certain minimal contact time of the composition with food product for occurrence of significant antimicrobial effect. The contact time can vary with concentration of the use composition, method of applying the use composition, temperature of the use composition, amount of soil on the food product, number of microorganisms on the food product, type of antimicrobial agent, or the like. Preferably the exposure time is at least about 5 to about 15 seconds.

15 A preferred method for washing food product employs a pressure spray including the stabilized composition. During application of the spray solution on the food product, the surface of the food product can be moved with mechanical action, preferably agitated, rubbed, brushed, etc. Agitation can be by physical scrubbing of the food product, through the action of the spray solution under pressure, through sonication, or by other methods. 20 Agitation increases the efficacy of the spray solution in killing micro-organisms, perhaps due to better exposure of the solution into the crevasses or small colonies containing the micro-organisms. The spray solution, before application, can also be heated to a temperature of about 15 to 20 °C, preferably about 20 to 60 °C to increase efficacy. The spray stabilized 25 composition can be left on the food product for a sufficient amount of time to suitably reduce the population of microorganisms, and then rinsed, drained, or evaporated off the food product.

30 Application of the material by spray can be accomplished using a manual spray wand application, an automatic spray of food product moving along a production line using multiple spray heads to ensure complete contact, or other spray apparatus. One preferred automatic spray application involves the use of a spray booth. The spray booth substantially

confines the sprayed composition to within the booth. The production line moves the food product through the entryway into the spray booth in which the food product is sprayed on all its exterior surfaces with sprays within the booth. After a complete coverage of the material and drainage of the material from the food product within the booth, the food product can
5 then exit the booth. The spray booth can include steam jets that can be used to apply the stabilized compositions of the invention. These steam jets can be used in combination with cooling water to ensure that the treatment reaching the food product surface is less than 65°C, preferably less than 60°C. The temperature of the spray on the food product is important to ensure that the food product is not substantially altered (cooked) by the temperature of the
10 spray. The spray pattern can be virtually any useful spray pattern.

Immersion a food product in a liquid stabilized composition can be accomplished by any of a variety of methods known to those of skill in the art. For example, the food product can be placed into a tank or bath containing the stabilized composition. Alternatively, the food product can be transported or processed in a flume of the stabilized composition. The washing solution is preferably agitated to increase the efficacy of the solution and the speed at which the solution reduces micro-organisms accompanying the food product. Agitation can be obtained by conventional methods, including ultrasonics, aeration by bubbling air through the solution, by mechanical methods, such as strainers, paddles, brushes, pump driven liquid jets, or by combinations of these methods. The washing solution can be heated to increase the efficacy of the solution in killing micro-organisms. After the food product has been immersed for a time sufficient for the desired antimicrobial effect, the food product can be removed from the bath or flume and the stabilized composition can be rinsed, drained, or evaporated off the food product.
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In another alternative embodiment of the present invention, the food product can be treated with a foaming version of the composition. The foam can be prepared by mixing foaming surfactants with the washing solution at time of use. The foaming surfactants can be nonionic, anionic or cationic in nature. Examples of useful surfactant types include, but are not limited to the following: alcohol ethoxylates, alcohol ethoxylate carboxylate, amine oxides, alkyl sulfates, alkyl ether sulfate, sulfonates, quaternary ammonium compounds,
25 alkyl sarcosines, betaines and alkyl amides. The foaming surfactant is typically mixed at time of use with the washing solution. Use solution levels of the foaming agents is from
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about 50 ppm to about 2.0 wt-%. At time of use, compressed air can be injected into the mixture, then applied to the food product surface through a foam application device such as a tank foamer or an aspirated wall mounted foamer.

In another alternative embodiment of the present invention, the food product can be
5 treated with a thickened or gelled version of the composition. In the thickened or gelled state
the washing solution remains in contact with the food product surface for longer periods of
time, thus increasing the antimicrobial efficacy. The thickened or gelled solution will also
adhere to vertical surfaces. The composition or the washing solution can be thickened or
gelled using existing technologies such as: xanthan gum, polymeric thickeners, cellulose
10 thickeners, or the like. Rod micelle forming systems such as amine oxides and anionic
counter ions could also be used. The thickeners or gel forming agents can be used either in
the concentrated product or mixing with the washing solution, at time of use. Typical use
levels of thickeners or gel agents range from about 100 ppm to about 10 wt-%.

15 It should be noted that, as used in this specification and the appended claims, the
singular forms "a," "an," and "the" include plural referents unless the content clearly dictates
otherwise. Thus, for example, reference to a composition containing "a compound" includes
a mixture of two or more compounds. It should also be noted that the term "or" is generally
employed in its sense including "and/or" unless the content clearly dictates otherwise.

20 All publications and patent applications in this specification are indicative of the level
of ordinary skill in the art to which this invention pertains.

The invention has been described with reference to various specific and preferred
embodiments and techniques. However, it should be understood that many variations and
modifications may be made while remaining within the spirit and scope of the invention.